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REE MINERALS IN CATALÃO II, GOIAS, BRASIL

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Abstract The REE minerals pyroxenites and sövites of Catalão II show a substantial enrichment in REE from the magmatic stage. The activity of carbonate and CO_3^{2-}/ PO_4^{3-} ratio have played an important role in the formation of REE-carbonate-phosphates, which are an intermediate form between REE-rich apatite and REE-rich carbonate. The magmatic enrichment in REE and Ti, favored by the presence of a carbonate phase, correlate to a high activity of CO_3^{2-} and activities of Ti and Na specially in the carbonatite. This feature explains the low enrichment in phosphate (apatite vein) in Catalão II compared to Catalão I, which is rich in apatite vein.
In the weathering stage, these minerals interact with the fluid surface and lose some of their REE and Ba. The exchange reactions between pyrochlore and ground water are generally consistent with relatively low pH, low activities of Na^+, Ca^{2+}, F^- and elevated activities of Ba^{2+} /or Ce^{3+}. Significant amounts of Ba were derived from barite dissolution with some silicate contribution, whereas the Ce might come, either from dissolved REE-carbonate minerals or from the pyrochlore themselves through selective immobilisation of Ce as Ce^{4+}.

Keywords: pyrochlore, REE- carbonate phosphates, niobium, carbonatite, Brazil.

1. Introduction

The alkaline-carbonatite complex of Catalão II has been the subject of only few mineralogical studies (Machado 1983) in comparison to Catalão I, its nearest neighbor, presently under operation (Baecker, 1983, Gomes et al. 1990, Danni et al. 1991 and Pereira, 1995). This difference is probably due to the structural organization of the Catalão II complex pipes, next to the simplest Catalão I dome structure, and - until recently - to the absence of mining works on this intrusion. The surface of the bodies presents a residual metric zone with magnetite in abundant large crystals (mm-cm) and weathered white pyrochlore. However, this complex has been an attractive target for a crystallochemical study of the evolution of pyrochlore and REE-carbonate phosphate.

2. Geological setting

The Catalão II carbonatite complex (18° 02' S, 47° 52' W, 5 x 2.7 km) is located in the province of alkaline-carbonatite "Alto Paranaíba", southeast of the state of Goiás and westwards of Minas Gerais, Brazil. It outcrops at about 20 km NE of the city of Catalão, along the road connecting São Paulo and Brasilia and at 10 km NW of the better known Catalão I complex. It lies at the northern end of the tectono-magmatic lineament that controls the development of most carbonatite complexes in the region: Tapira, Araxá, Salitre, Serra Negra and Catalão I (Gomes et al. 1990). The Catalão II carbonatite complex has been dated to 83 Ma (Rb/Sr) (Machado 1983). It intrudes metasediments of the group Araxá Mesoproterozoic (Fig.1). These metasediments (quartzite, micaschists) are fenitized at the contact with intrusive bodies (sodic to potassic fenites on a south to north trend).
The structural organization of Catalão II (Fig. 1), where a tangle of veins and dykes can be divided into two "pipes" separated by a few kilometers (Machado 1983), differs from the dome of Catalão I. Geomorphic expression is also much more discreet than in the case of Catalão I: it appears only at 900-1000 m altitude, in a leveled landscape, covered by a shrub savanna (cerrado).
The most comprehensive study concerned drill-hole C3B1, located at about 175m north of the pipe). The drill first intersected several tens of meters of reddish-yellow clay soil, with frequent passages rich in agnetite. Between 30 m and 40 m, decimetric levels of red cavernous siliceous crust, with rare baryte veins. In addition, the profile becomes progressively enriched in apatite, dispersed in a yellowish-brown clay matrix.
The first not weathered carbonatite occurs only after 52 m and the completely unaltered rock at 60 m only. The six drills from 150 to 450 m (four in the northern shaft and two in the south) made by the mining company "Mineração Catalão of Goiás" and studied in great detail by Machado 1983, showed the presence of five successive magmatic facies: pyroxenites, syenites, phoscorites, carbonatites and lamprophyres.

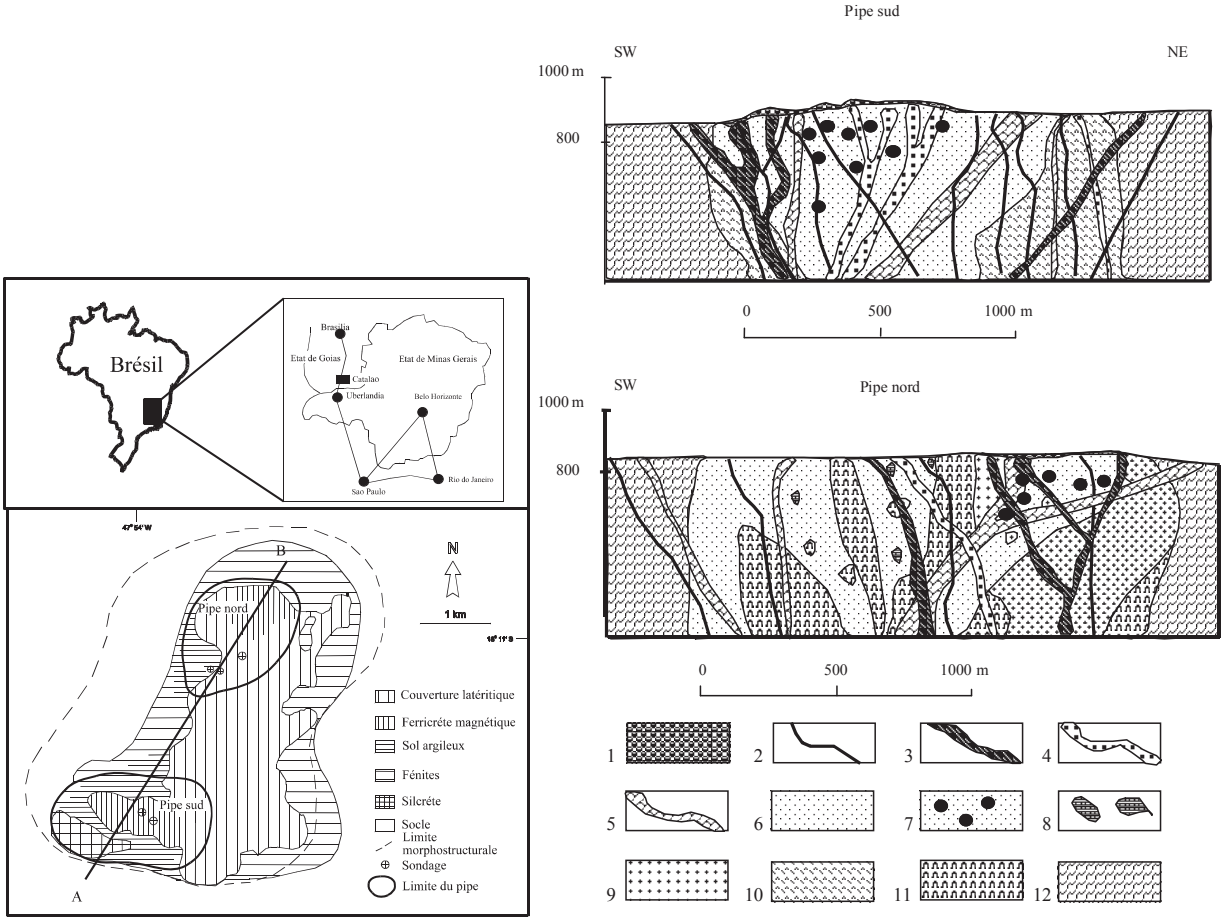

Fig. 1. The Catalão II complex localization and schematic section of the"Catalão II" Nb deposit; section drafted after drilling data and showing relationships between the different lithologic facies (Machado, 1991 and Rochas et al. 2001). 1: Blocks of residual magnetite; 2: lamprophyre dyke; 3: alvikite and béforsite dyke; 4: ankerite sövite dykes; 5: sövite; 6: silico-sövite; 7: carbonatite-rich pyrochlore; 8: phoscorite; 9: syenite; 10: altered pyroxenite glimmerite; 11: unaltered pyroxenite and 12: Mesoproterozoic host rocks (quartzite and mica schists).

3. Mineral geochemistry

3.1 Pyrochlore

The pyrochlore (in mm up to cm crystals) is associated with magnetite in carbonatites and with phlogopite, magnetite and apatite in pyroxenites. Sometimes, pyrochlore is surrounded by zirconolite, baddeleyite or columbo-tantalite. Perovskite and Nb-ilmenite surround or are included in the pyrochlore from pyroxenite or carbonatite.

The structural formula is close to the ideal formula $(Ca,Na)_2Nb_2O_6(OH, F)$. Compared to unweathered pyrochlore, structural formulas of weathered pyrochlore indicate major loss of Na, Ca, F, and major increase in Ba or Ce (Nasraoui and Bilal, 1999). These changes are correlated to an increase in the A-site vacancies and hydration, as suggested by low analytical totals (Fig. 2) Weathering involves considerable cation exchange for Ba and Ce, generating hydrated and deficient pyrochlores of B*ario* and C*erio-pyrochlore* compositions.

However, there is an unweathered rich REE pyrochlore without the A-site vacancy (Fig. 2).

The REE-rich pyrochlore associated with Ti-rich pyrochlore (Fig. 3), this association is unusual for a pyrochlore. Note that the REE plots are very similar for this phase so suggests that it is only phase but with compositional zoning in elements not including REE.

The pyrochlores from Catalão II involve coupled substitutions:

$$Na^{+}+REE^{3+} = 2Ca^{2+} \quad (1)$$
$$2Ti^{4+}+REE^{3+} = Na^{+} +2Nb^{5+} \quad (2)$$
$$Ti^{4+}+REE^{3+} = Ca^{2+} +Nb^{5+} \quad (3)$$

The substitutions (1) and (2) can generate REE-rich pyrochlore and the substitution (3) with Na constant is involving the Ti-rich pyrochlore.

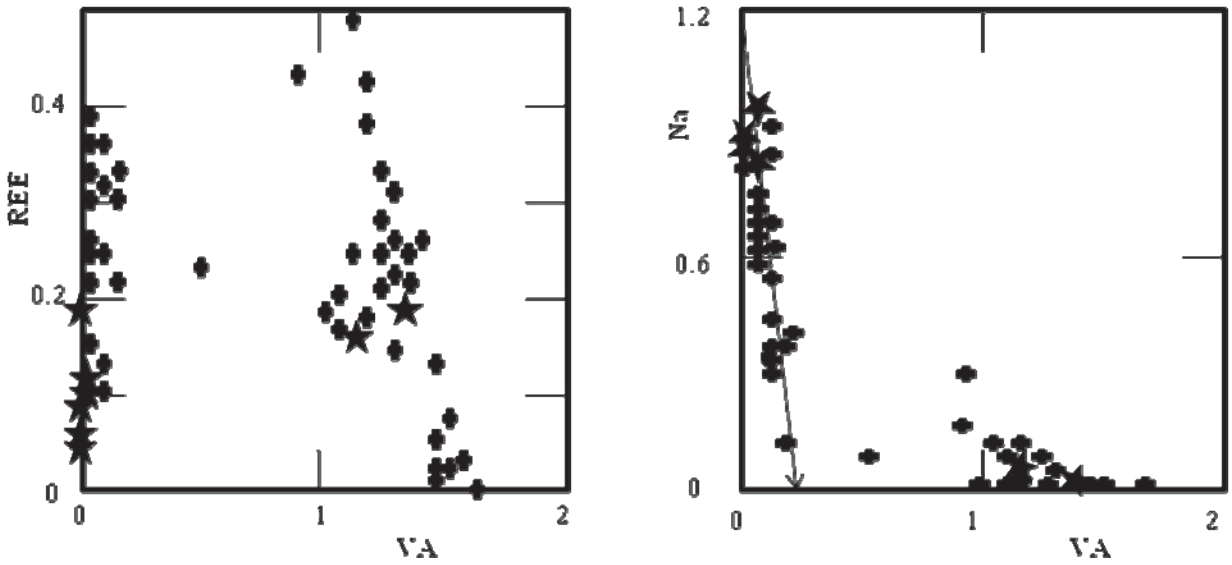

Fig. 2. Na and REE versus VA distribution in pyrochlore, in cations per unit formula. VA refers to A site vacancy.

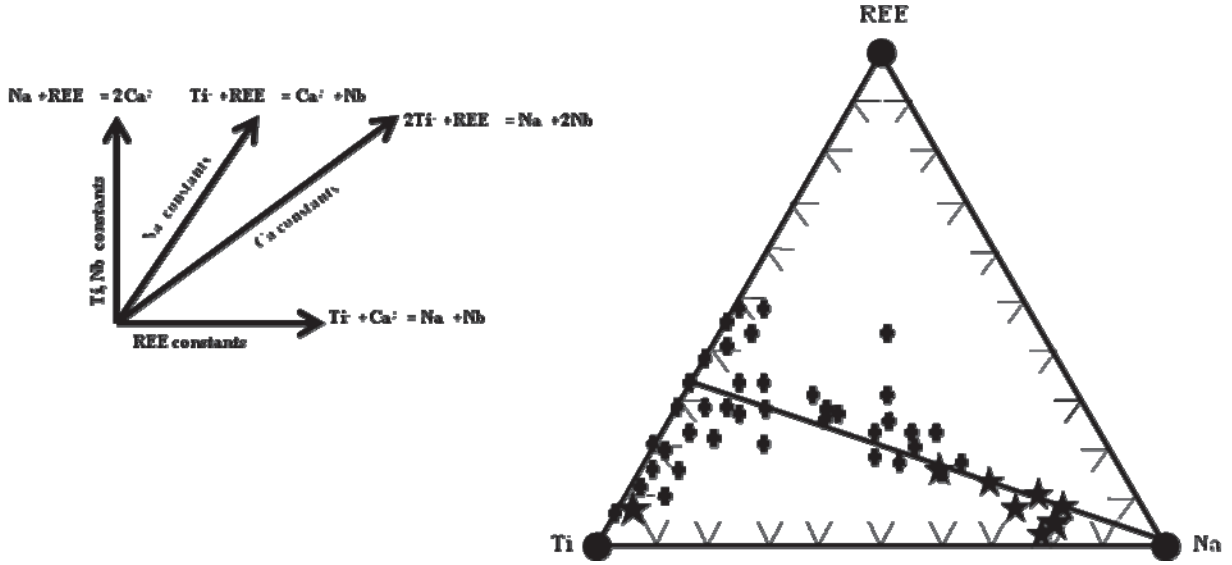

Fig. 3. Pyrochlore distribution in ternary diagram Ti-REE-Na (a/f.u.) from sövite (star) and pyroxenite (cross) of Catalão II carbonatite complex. The planar vector representation indicates different substitution mechanisms.

3.2 REE- carbonate phosphates

The infra-red (IR) study confirms the presence of carbonate ions. The peaks at 1435 cm^{-1} and 1455cm^{-1} represents the vibration of the double valence (ν_3) of the C – O group and the peak at 870 cm^{-1} the vibration (ν_2) of CO_3^{2-}. Elliott (1965) also showed that, compared with the free carbonate ion, the carbonate ion in apatite is distorted and although the carbonate ion of apatite type B is oriented parallel to the c axis, the carbonate ion of apatite A is approximately perpendicular to the c axis.

A site: The REEs in Ca that crystallized from H_2O bearing phosphate fluoride melts where compensated in charge by concomitant substitutions of both Si for P and Na for Ca. The distribution Nb versus Ti ions show the substitution of these two ions from the sövite. The compositional range also shows a deviation from the one recorded for pyroxenite (Fig. 4C).

B-site carbonate bearing apatite, involving replacement of the PO_4^{3-} group by CO_3^{2-} is now well established (Ivanova et al. 2001). Polarized IR studies suggested that the orientation of the CO_3^{2-} ion lies in the position of the sloping face of the replaced PO_4^{3-} tetrahedron (Elliott, 1965).

The charge compensating mechanisms have been proposed for the incorporation of CO_3^{2-} ion into the PO_4^{3-} sites:

$$CO_3^{2-} + Na^+ = PO_4^{3-} + Ca^{2+} \quad (4)$$

$$REE^{3+} + Na^+ = 2Ca^{2+} \quad (5)$$

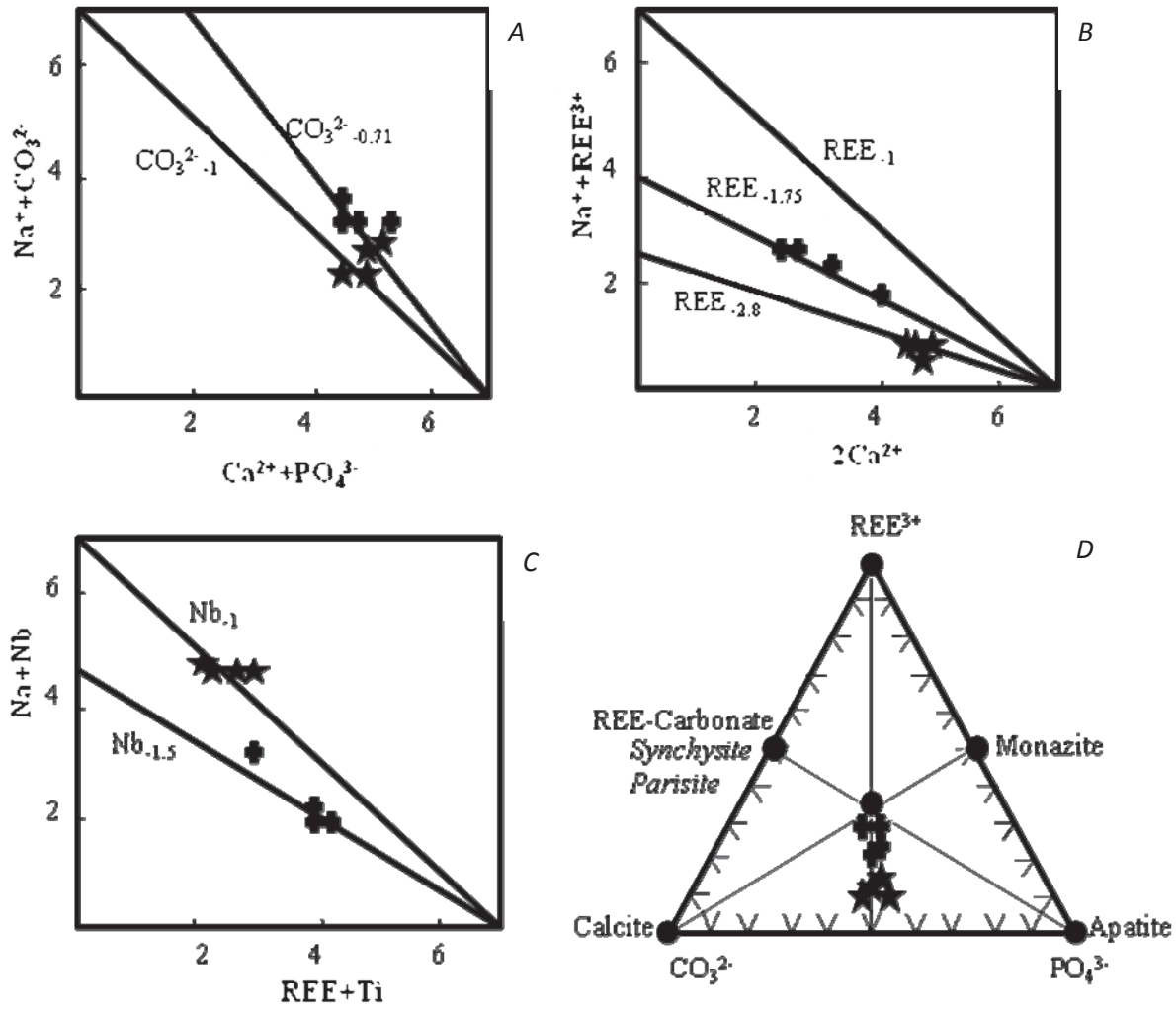

Fig. 4. Relationship between $CO3^{2-}$, $PO4^{3-}$ and $REE^{3+,}$ and Nb-Ti in REE-carbonate-phosphate. Star symbols: sövite; cross symbols: pyroxenite.

The coupled Substitutions (4) and (5) involving simultaneous replacement of Na^+ for Ca^+ may also be proposed (Fig. 4). However, excess charge may be subsequently adjusted by CO_3OH^{3-} partly accompanied by the REE in the Ca site. The presence of F in all REE-carbonate phosphate indicated probably a substitution (6) of fluorine and carbonate.

$$CO_3^{2-} + F^- = PO_4^{3-} \qquad (6)$$

The tetravalent carbon substituted for pentavalent phosphorus and a F^- in excess has replaced one O^{2-}in structure. The substitution mechanism was found within the hydroxyapatite group (Sommerauer and Katz-Lehnert, 1985), yielding the following simplified formula:
$(Ca, Na, LREE)_{10}\ (F, CO_3)_x(PO_4)_{6-x}(OH, F)_2$.

4. Conclusions

We have two unaltered pyrochlore REE-rich and Ti-rich without VA vacancy site. The magmatic enrichment in REE and Ti favoured by the presence of a carbonate phase, correlate with a high activity of CO_3^{2-}, activity of Ti and activity of Na^+ specially in the carbonatite. This feature explains the low enrichment in phosphate (apatite veins) in Catalão II compared to Catalão I, which is rich in apatite veins. The activity of carbonate and ratio CO_3^{2-}/ PO_4^{3-} have played an important role in the formation of REE-carbonate phosphate, which are an intermediate form between REE-rich apatite and REE-rich carbonate.
In the weathering stage, the exchange reactions between pyrochlore and ground water are generally consistent with relatively low pH, low activities of Na^+, Ca^{2+}, F^- and elevated activities of Ba^{2+} /or of $Ce^{3+.}$ Significant amounts of Ba derived from baryte dissolution with some silicate contribution, whereas the Ce might come, either from dissolved REE-carbonate minerals or from the pyrochlores themselves.

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